

## Supplementary Material

### Impact of (nano)formulations on the distribution and wash off of copper pesticides and fertilisers applied on citrus leaves.

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**Table S1. Distribution of Cu (%) in four size fractions for the nine Cu formulations studied**

Determined by membrane filtration at 3 concentrations (2 g/L, 100 and 10 mg/L). Results were statistically similar at the three concentration levels and only results are shown for 2 g/L (corresponding to the concentration applied to the leaves).

0: means < 0.3% of total Cu.

	Si50	Si500	CuSO <sub>4</sub>	Tribasic	nCuO	Kocide	Cu(OH) <sub>2</sub>	Champ	GO
> 0.45 µm	100	100	0.7	98.6	100	81.8	100	97.6	47.2
0.45-0.1 µm	0	0	-0.3 <sup>A</sup>	1.4	0	1.1	0	1.1	0
< 100 nm	0	0	5.7	0	0	17.1	0	1.3	1.5
< 3kDa	0	0	93.9	0	0	0.0	0	0.0	51.3

<sup>A</sup> Result within the variability range and kept to maintain 100% for the mass balance

**Table S2. Size characteristics derived from SEM images of the particles deposited on the citrus leaves before washing (including pictures shown on Figure S5).**

SEM images show aggregates of primary particles covering a wide range of size. Primary particles were the focus of the size measurement.

N is the number of particles measured on at least two images taken at x 20000 magnification and analysed using ImageJ. For Si50, CuSO<sub>4</sub> and GO, there were no suitable particles visible for measurement.

	Mean (nm)	Standard deviation	Median (nm)	Min (nm)	Max (nm)	N
Si50	-	-	-	-	-	-
Si500	579.14	27.97	563.49	481.19	639.91	58
CuSO <sub>4</sub>	-	-	-	-	-	-
Tribasic length	819.25	227.63	756.74	329.05	2019.41	140
Tribasic width	137.06	29.52	131.26	61.67	235.47	140
nCuO	56.18	9.85	54.64	37.84	80.02	100
Kocide	998.01	512.10	904.25	305.27	2790.27	58
Cu(OH) <sub>2</sub> length	1250.54	418.61	1189.19	363.19	2527.76	80
Cu(OH) <sub>2</sub> width	168.26	41.83	162.03	58.97	292.11	81
ChampDP length	772.00	205.64	745.47	409.56	1413.14	101
ChampDP width	114.17	45.92	104.17	39.19	295.59	102
GO	-	-	-	-	-	-

Figure S1. Experimental set up

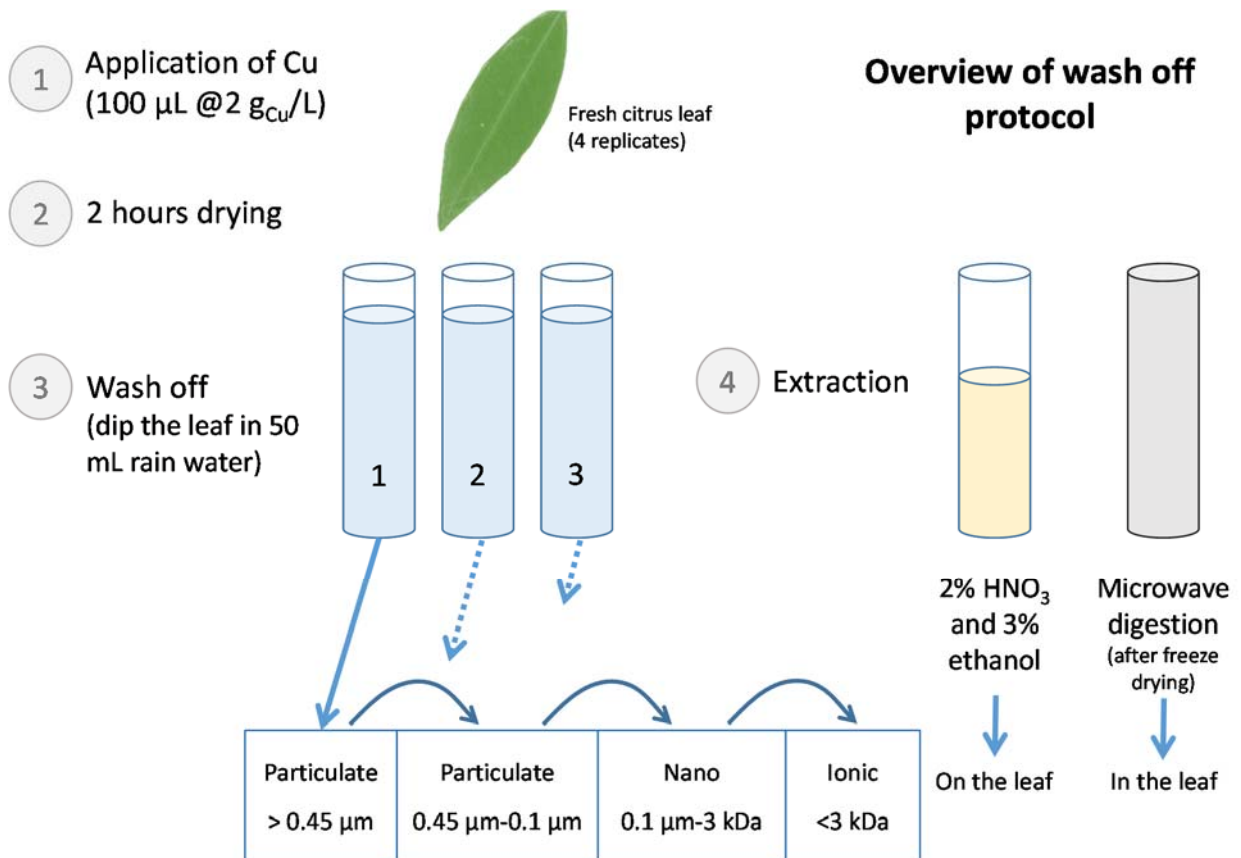
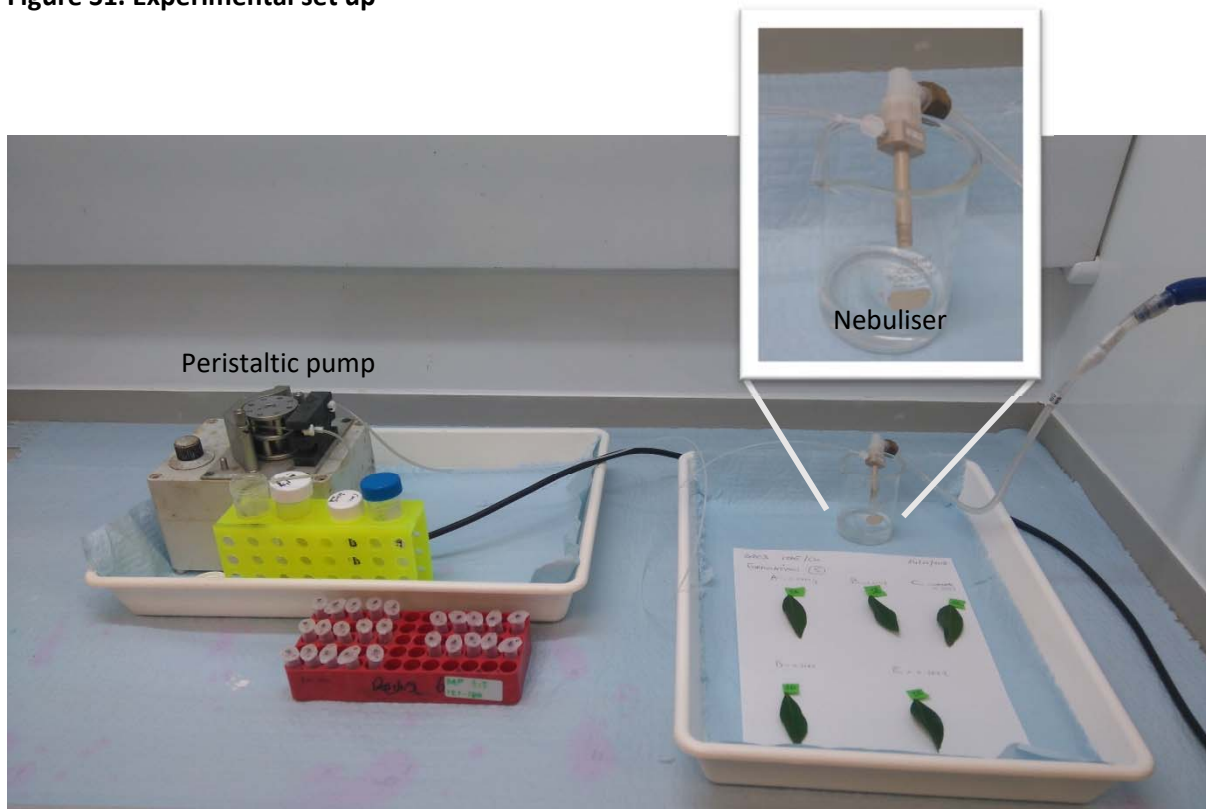
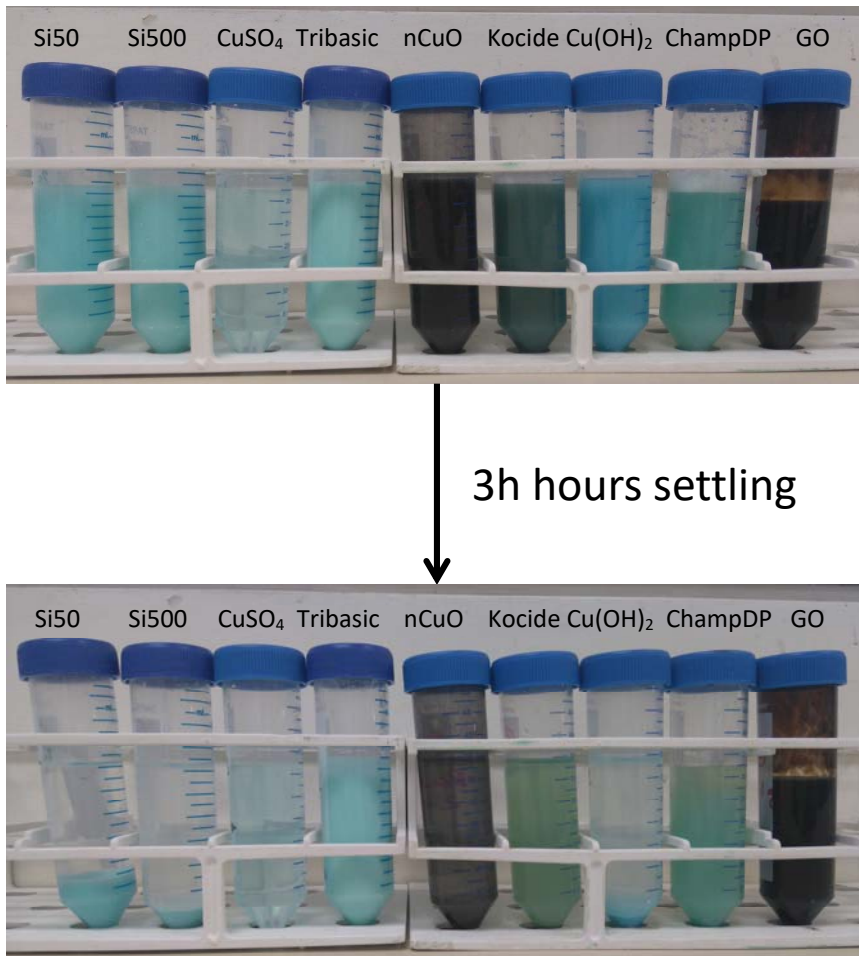


Figure S2. Nine formulations of Cu freshly prepared (a) and after 3h settling (b)



**Figure S3. pH, Z-average, Pdl and  $\zeta$ -potential measured at 10 (light grey) and 100 mg/L (dark grey)**  
 Suspensions were prepared in rain water as used in the wash off experiments.

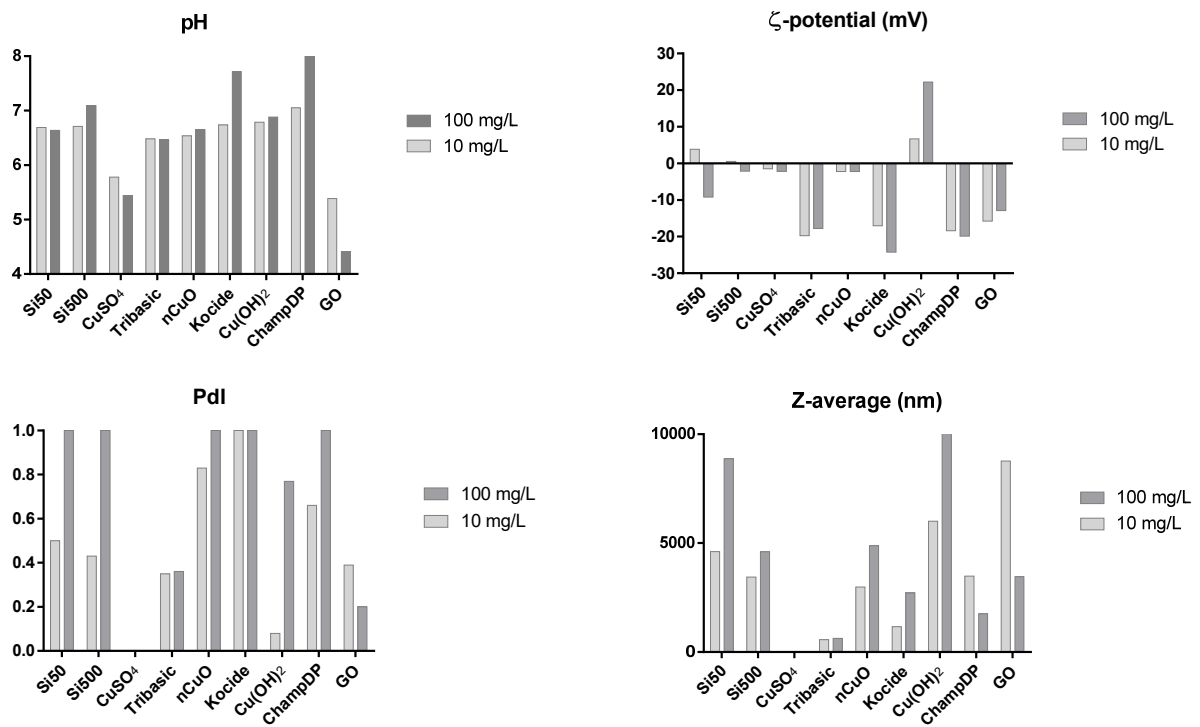
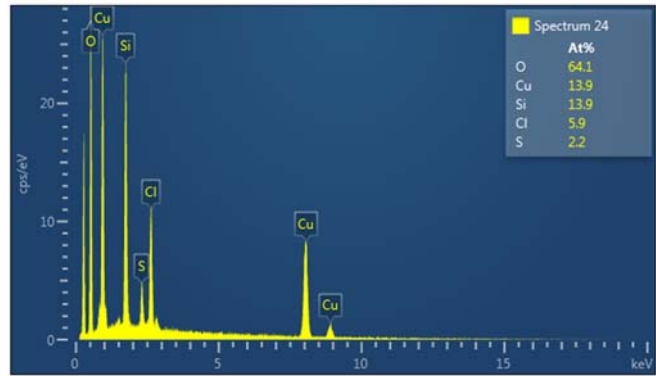
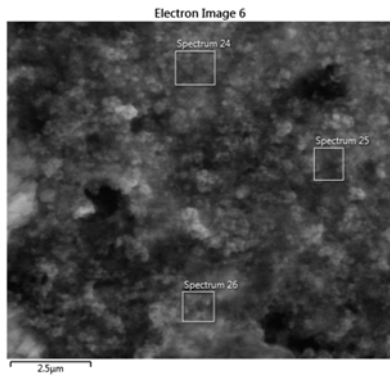
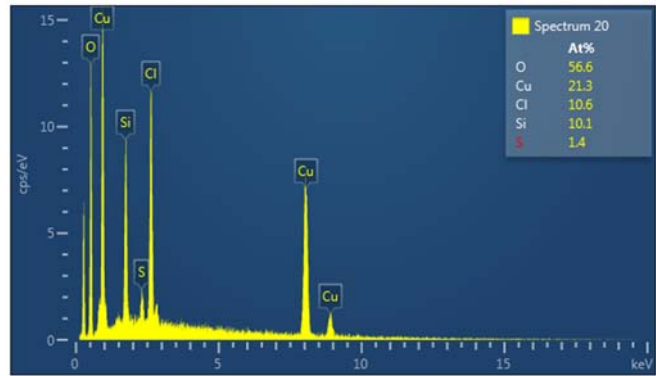
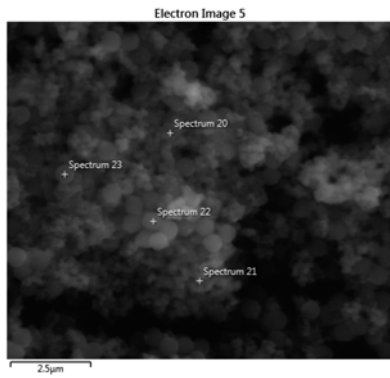


Figure S4. Examples of energy-dispersive X-ray spectra

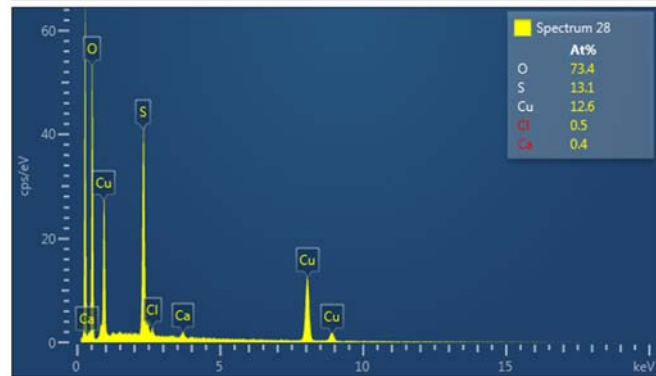
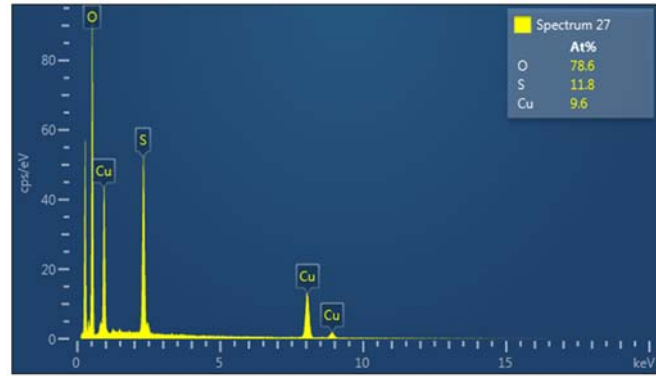
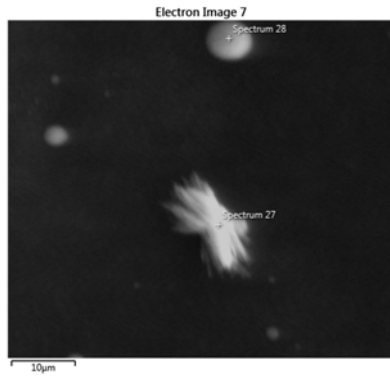
Si50



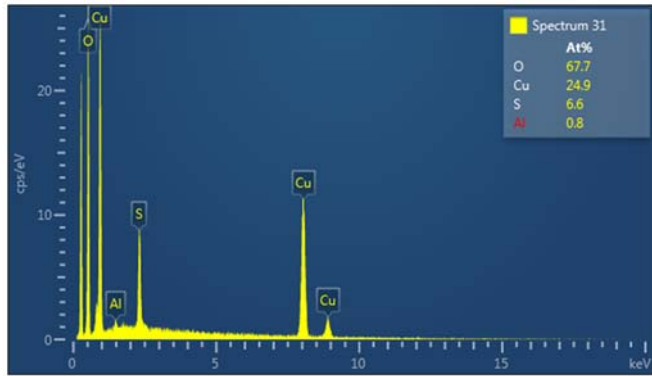
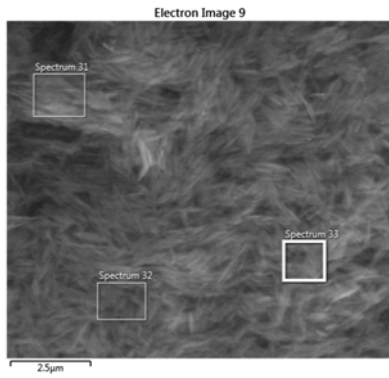
Si500



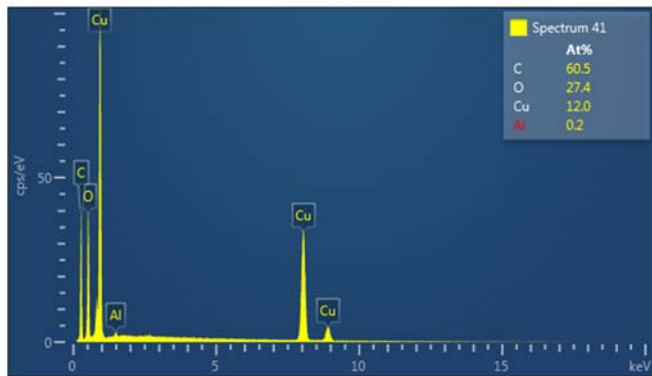
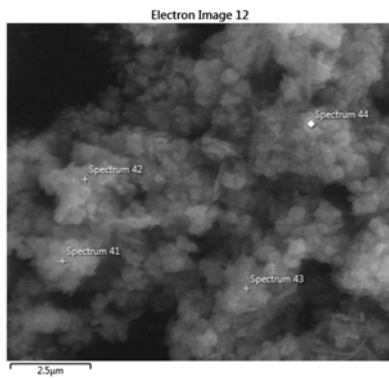
CuSO<sub>4</sub>



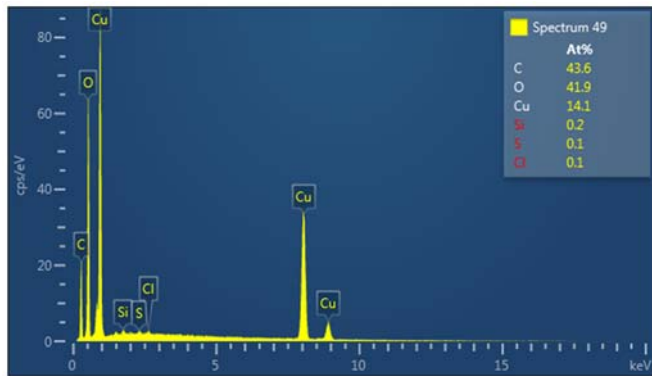
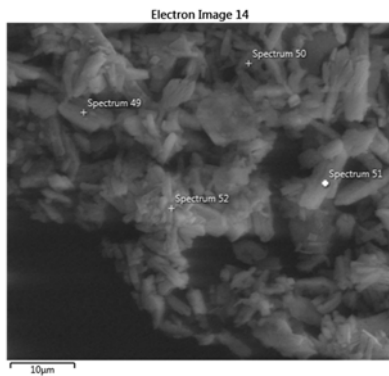
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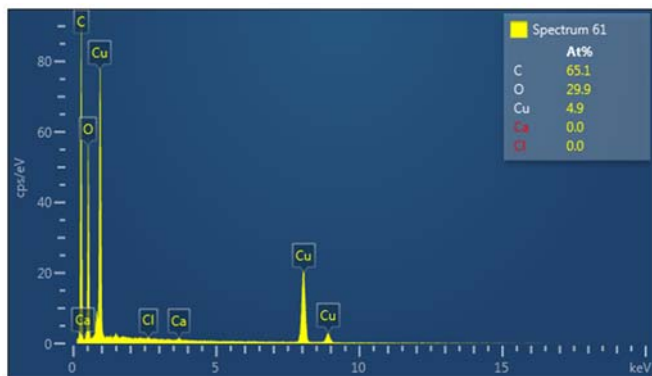
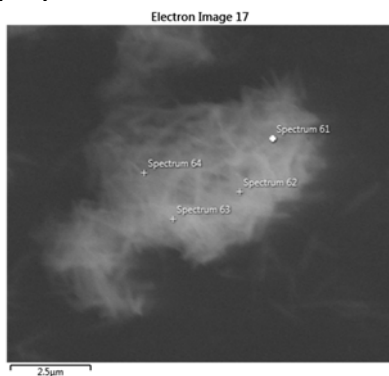
### nCuO



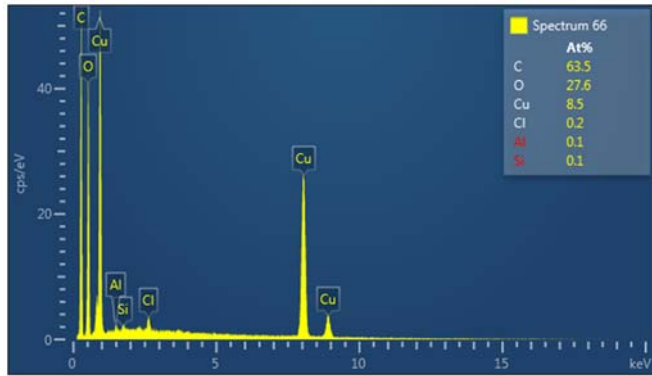
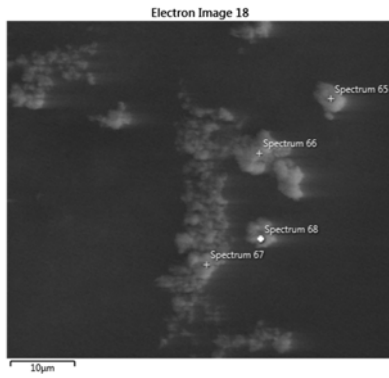
### Kocide



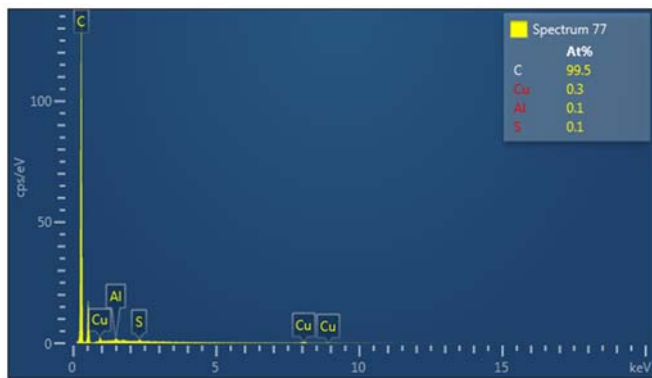
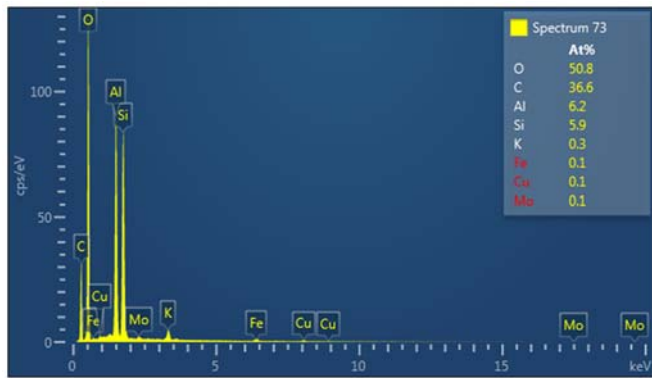
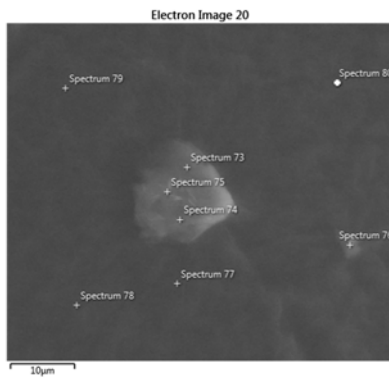
### Cu(OH)<sub>2</sub>



## ChampDP



## GO



## Blank (carbon tape)

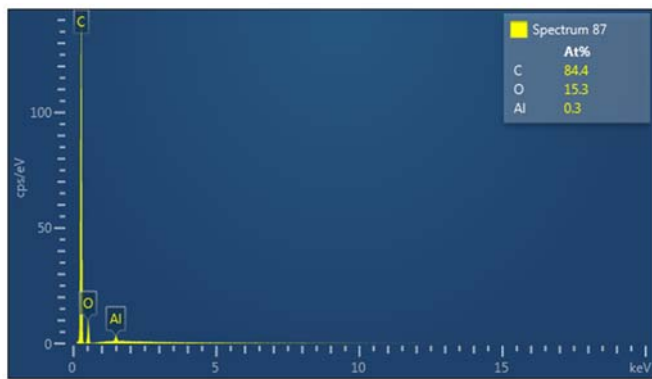
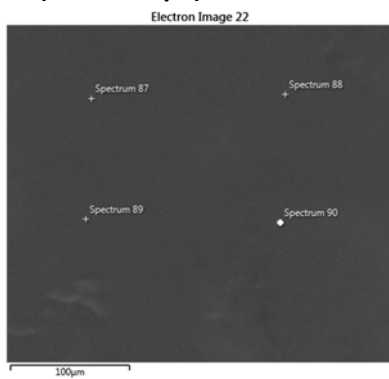




Figure S5. Optical microscope images at a magnification x20 (scale bar is 500  $\mu\text{m}$ ).

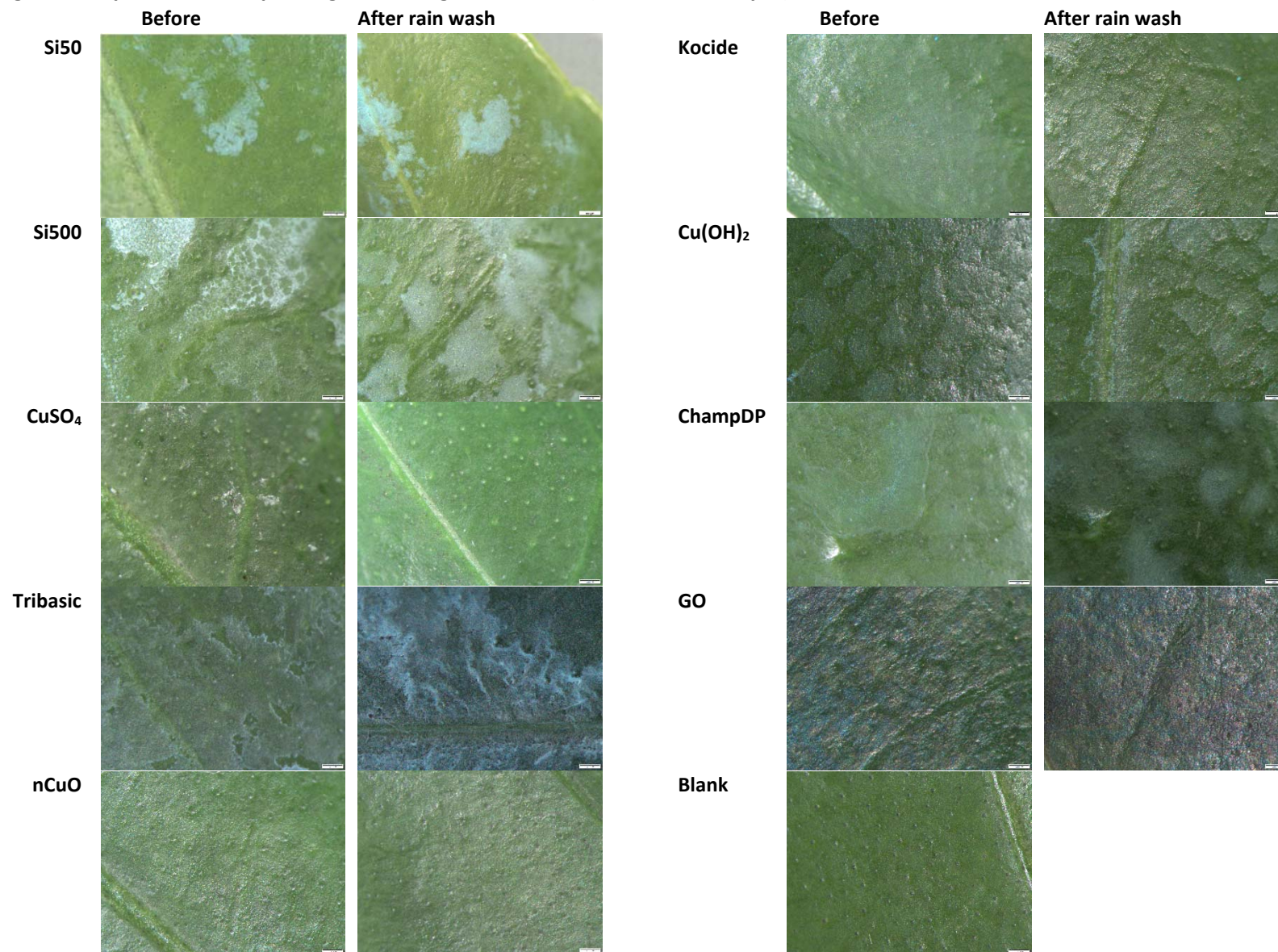
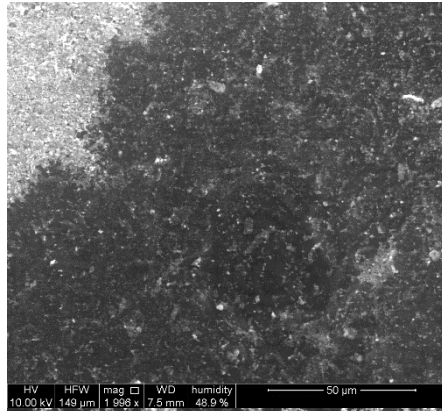
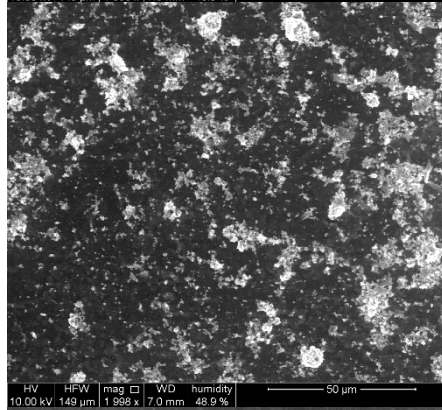


Figure S6. Electron microscope images of leaf surface sprayed with nine formulations of Cu. Magnification x2000 (the scale bar is 50  $\mu$ m).

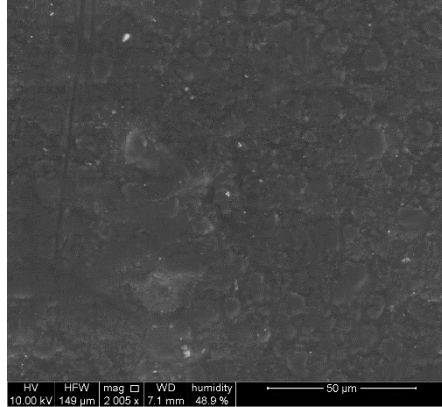
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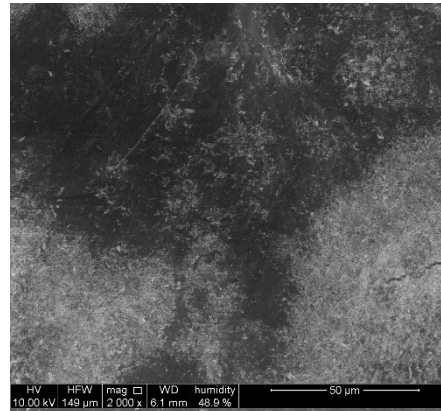
Si500



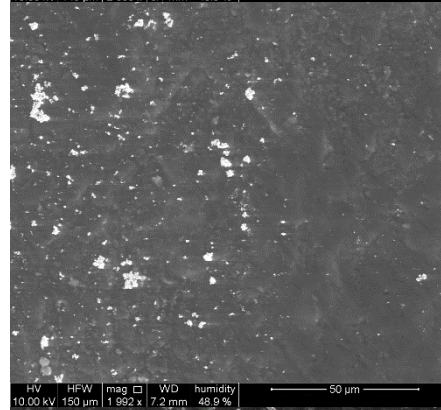
CuSO<sub>4</sub>



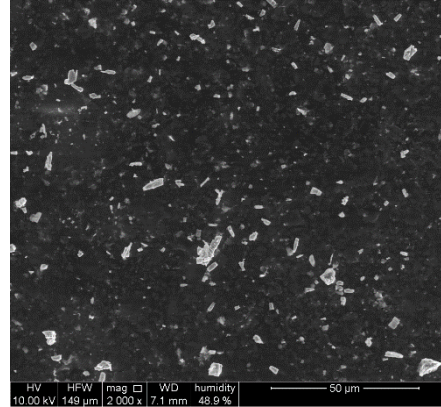
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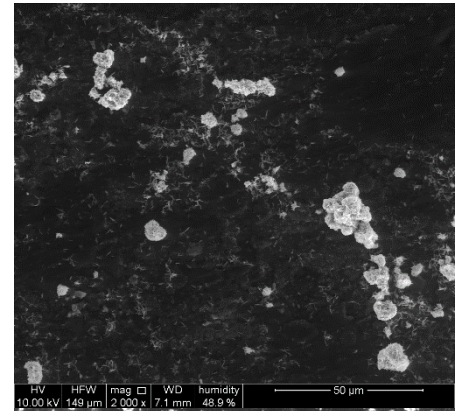
nCuO



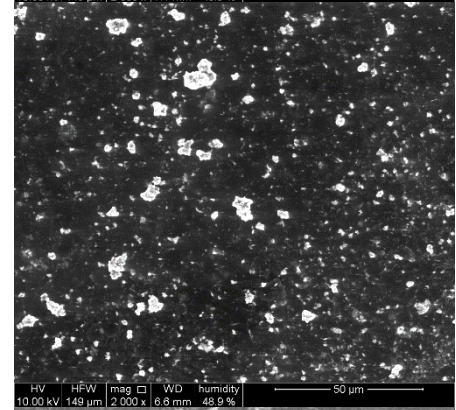
Kocide



Cu(OH)<sub>2</sub>



Champ



GO

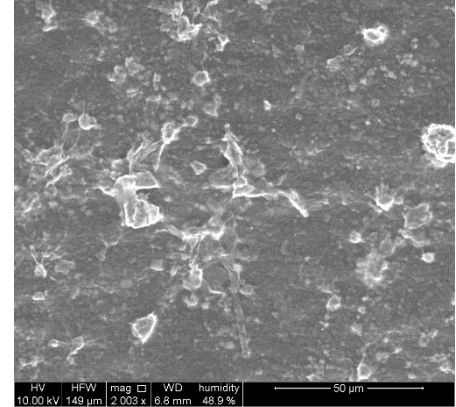
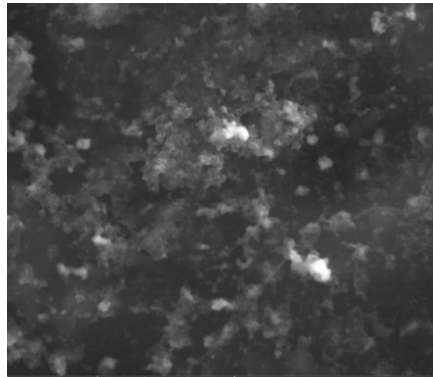


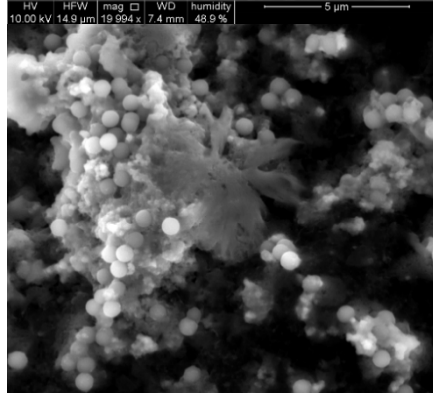
Figure S7. Electron microscope images of leaf surface sprayed with nine formulations of Cu. Magnification x20000 (the scale bar is 5  $\mu$ m).

Si50



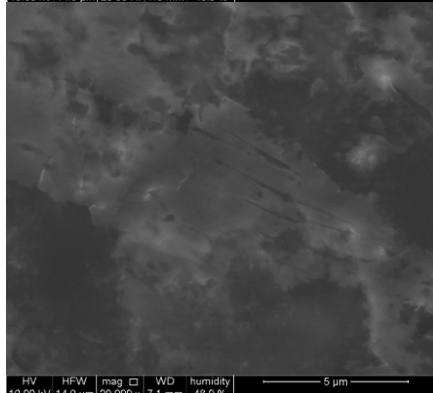
HV HFW mag WD humidity  
10.00 kV 14.9  $\mu$ m 19,994 x 7.4 mm 48.9 %

Si500



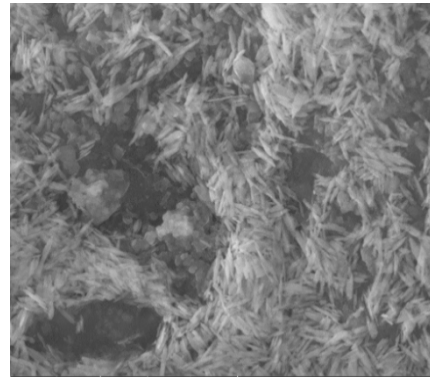
HV HFW mag WD humidity  
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CuSO<sub>4</sub>



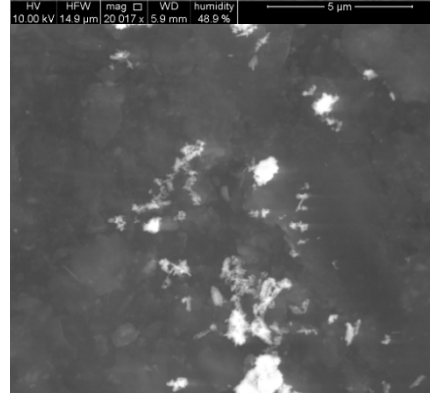
HV HFW mag WD humidity  
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Tribasic



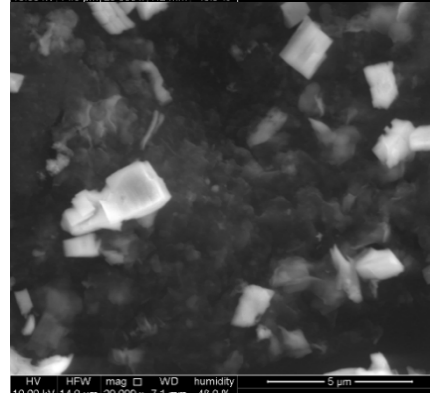
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nCuO



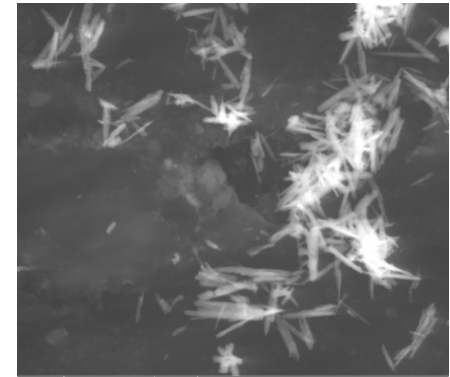
HV HFW mag WD humidity  
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Kocide



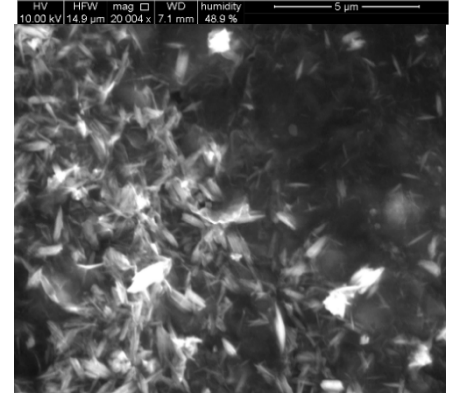
HV HFW mag WD humidity  
10.00 kV 14.9  $\mu$ m 20,000 x 7.1 mm 48.9 %

Cu(OH)<sub>2</sub>



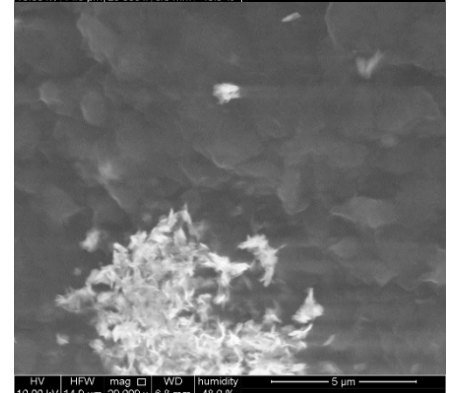
HV HFW mag WD humidity  
10.00 kV 14.9  $\mu$ m 20,004 x 7.1 mm 48.9 %

Champ



HV HFW mag WD humidity  
10.00 kV 14.9  $\mu$ m 20,000 x 6.8 mm 48.9 %

GO



HV HFW mag WD humidity  
10.00 kV 14.9  $\mu$ m 20,000 x 6.8 mm 48.9 %

**Figure S8. Distribution of Cu in the successive rain wash solutions (W1, W2, W3), acid wash (AW) and in the leaves (all the data is combined on Figure 3 shown in the main document).**

Bars with letters in common belong to groups that are non-statistically different.

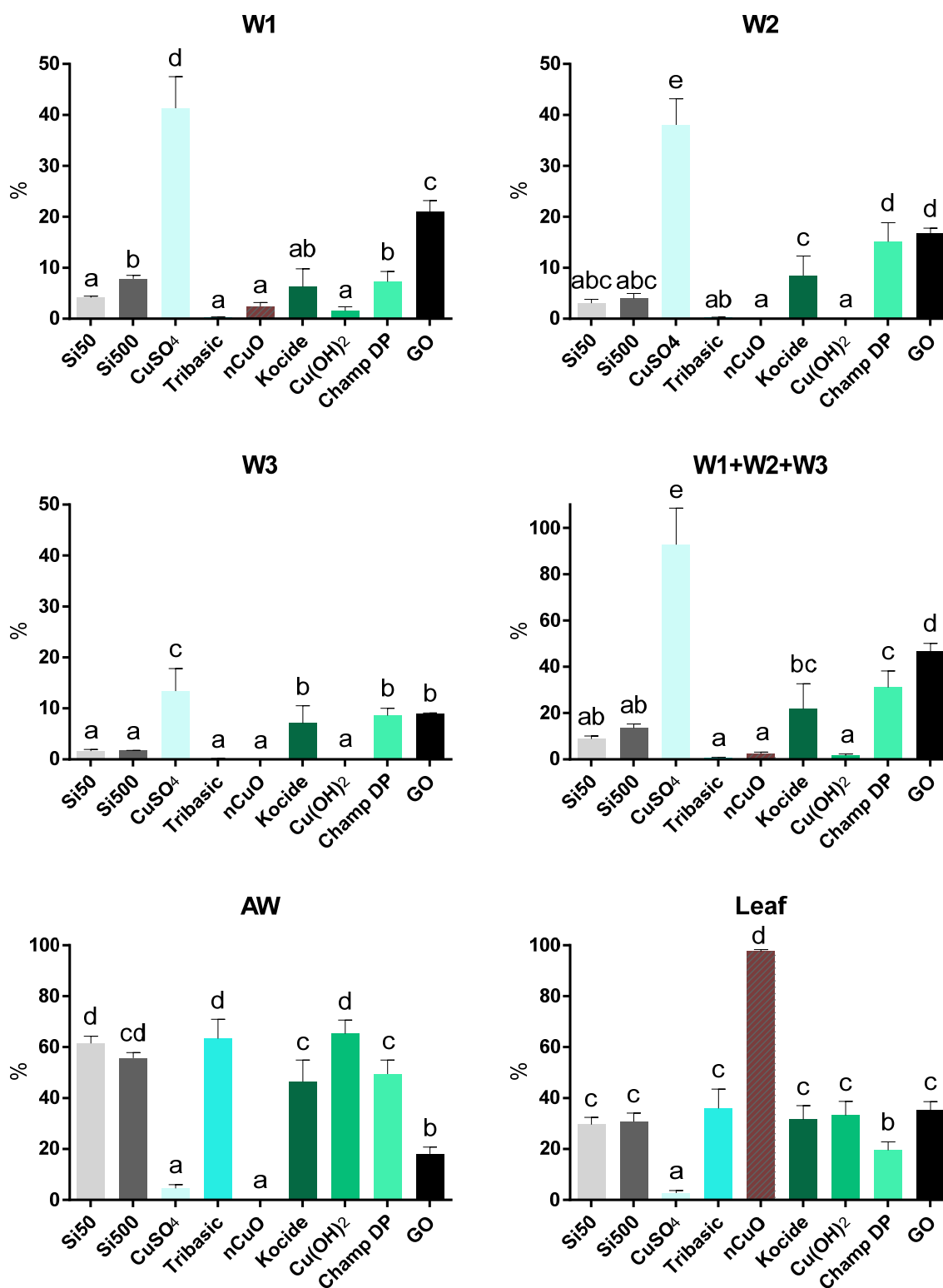
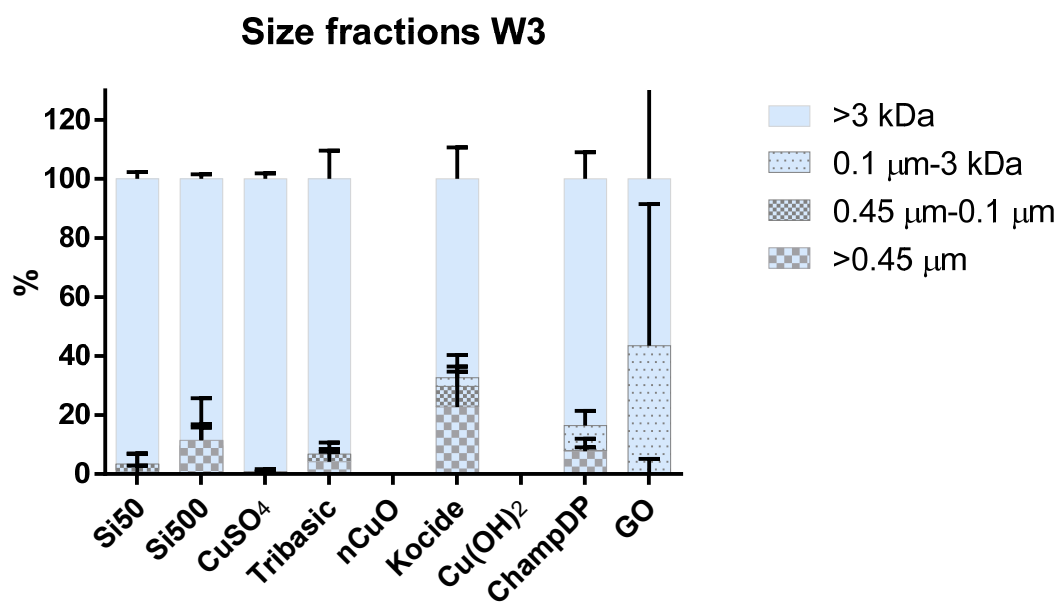
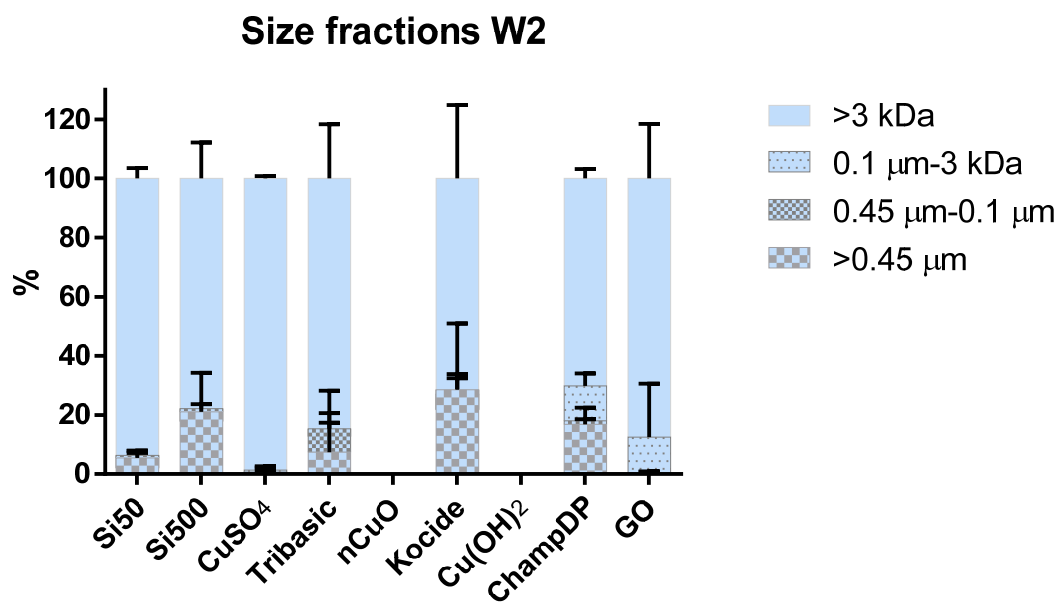


Figure S9. Distribution of Cu (%) in the second and third rain wash solutions (W2 and W3) and acid wash (AW) among four size fractions: > 45  $\mu\text{m}$ , 45-0.1  $\mu\text{m}$ , <0.1  $\mu\text{m}$  and 3kDa Errors bars represent the standard deviation (n=4).



**Figure S10. Distribution of Cu in four size fractions in W1 (all the data is combined on Figure 3 shown in the main document).**

Bars with letters in common belong to groups that are non-statistically different.

